

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 18/80, 18/28, 77/458, C09J 7/02		A1	(11) International Publication Number: WO 96/30426
			(43) International Publication Date: 3 October 1996 (03.10.96)

(21) International Application Number: PCT/US96/02083	(81) Designated States: CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 14 February 1996 (14.02.96)	
(30) Priority Data: 08/410,363 24 March 1995 (24.03.95) US 08/428,643 25 April 1995 (25.04.95) US	Published <i>With international search report.</i>
(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	
(72) Inventors: LEIR, Charles, M.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). BRONN, William, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	
(74) Agents: O'SHAUGHNESSY, Christine, T. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	

(54) Title: DIBLOCK AND TRIBLOCK POLYDIORGANOSILOXANE-POLYUREA BLOCK COPOLYMERS

(57) Abstract

Diblock (B-A) and triblock (B-A-B) polydiorganosiloxane-polyurea block copolymers comprise non-functional polydiorganosiloxane endblock B and polyurea block A. When used to provide release coatings, the block copolymers allow for easier release compared to traditional block copolymers of the (AB)_n type having comparable amounts of polydiorganosiloxane. Articles incorporating the copolymers as a release material are also disclosed.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

DIBLOCK AND TRIBLOCK POLYDIORGANOSILOXANE-POLYUREA
BLOCK COPOLYMERS

5 FIELD OF THE INVENTION

The present invention relates generally to polydiorganosiloxane-polyurea materials and, more specifically, to diblock and triblock copolymers thereof. The invention further relates to release materials based on these block copolymers as well as various articles comprising the block copolymers.

10 BACKGROUND OF THE INVENTION

Pressure sensitive adhesive (PSA) articles such as tapes, labels and other types of PSA-coated sheets, often require the use of either a release liner or a backing having a low adhesion backsize (LAB). Release liners and LABs provide a surface to which the adhesive does not permanently adhere, so that the 15 adhesive releases therefrom prior to use.

A backing having a LAB is particularly useful for providing an adhesive article such as a tape in roll form. In this case, adhesive is coated onto the side of the backing opposite the LAB so that when the adhesive coated backing is rolled, the adhesive contacts the LAB. The adhesive adheres well enough to the 20 LAB so that the roll does not come undone or "telescope", yet not so well that the tape cannot be unrolled.

Release liners may be used in a variety of ways to provide numerous types of adhesive articles. In some cases, the release liner functions as a support for a layer of adhesive. For example, a layer of adhesive may be coated onto the 25 release surface of the release liner to provide a transfer tape. In this case, the backside of the release liner may also have a LAB so that the transfer tape may be provided in roll form. In other cases, the release liner functions as a protective surface for the adhesive. For example, the release liner may be releasably adhered to the adhesive surface of a tape, label or other adhesive

article. The release liner is stripped from the adhesive article prior to application of the article to a surface.

The release liner or LAB comprises a release coating which is expected to provide an appropriate level of release from the adhesive of interest. The level of release is measured by the amount of force required to remove the release liner or LAB from the adhesive. Release levels within the range of 1.0 N/dm to 5 40 N/dm are typical for LABs used to provide adhesive articles in roll form. Release levels below 2.0 N/dm are generally preferred for release liners to provide smooth and easy release and are considered to be "premium".

10 Release coatings may comprise a wide variety of materials such as silicones, epoxysilicones, polyolefins (such as polyethylene and polypropylene), fluorocarbon polymers, acrylic polymers and copolymers, urethane polymers and copolymers, and the like. Further discussion of release coatings can be found in Handbook of Pressure Sensitive Adhesives, Satas, 1989, Van Nostrand Reinhold, 15 pages 585-626.

One type of release coating that is known to be suitable for a wide variety of PSAs comprises polydiorganosiloxane-polyurea segmented block copolymers of the (AB)_n type. U.S. Patent No. 5,214,119 (Leir) describes such an (AB)_n 20 segmented block copolymer wherein A represents an polydiorganosiloxane segment and B represents a polyurea segment. This reference discloses that the segmented copolymers may be tailored to have a wide range of release properties through variation in the ratio of segments, the nature of the chain extenders used to form the segments, and the molecular weight of the polydiorganosiloxane segment.

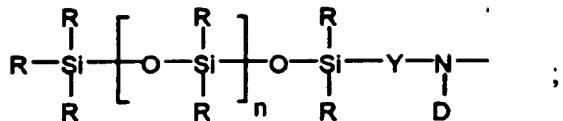
25 While the aforementioned release coatings based on (AB)_n block copolymers have proven acceptable for numerous applications, other release coatings providing advantages over the prior art are sought.

SUMMARY OF THE INVENTION

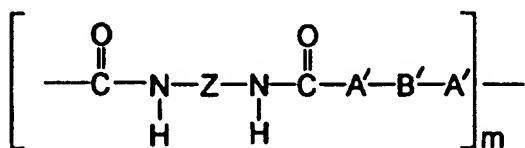
The present invention provides diblock (B-A) and triblock (B-A-B) polydiorganosiloxane-polyurea block copolymers which may be used, for example, to provide release materials. In general, mixtures of diblock and triblock copolymers are typically provided, the mixture preferably being predominantly triblock (B-A-B) copolymer. In these block copolymers, B comprises a non-functional polydiorganosiloxane endblock and A comprises a polyurea block. As used herein, the term "non-functional" means that the block is non-reactive to isocyanate. The term "polyurea block" is defined as a block having at least one urea, urethane, or thiourea moiety attached to the block.

Surprisingly, diblock and triblock copolymers of the present invention can provide unique advantages over $(AB)_n$ type block copolymers where the polydiorganosiloxane block (B) is typically internal to the block copolymer. For example, when release coatings are prepared, the B-A diblock and B-A-B triblock copolymers allow for easier release compared to traditional block copolymers of the $(AB)_n$ type having comparable amounts of polydiorganosiloxane. Furthermore, block copolymers of the present invention comprising relatively low levels of the B segment provide release levels that are typically only exhibited by 100% silicone release coatings. Furthermore, the B-A diblock and B-A-B triblock copolymers may be readily tailored for specific applications by incorporating various groups into the A segment. This ability to tailor the block copolymer allows it to be used in a variety of applications including, for example, protective coatings and protective films.

In one embodiment, diblock and triblock copolymers of the present invention may be described by the formula B-A-X wherein B comprises a non-functional polydiorganosiloxane endblock, A comprises a polyurea block, and X is selected from the group consisting of hydrogen, a non-functional polydiorganosiloxane endblock, or an isocyanate radical. More preferably, B has the structure:

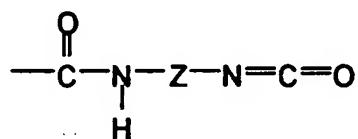


and A has the structure:

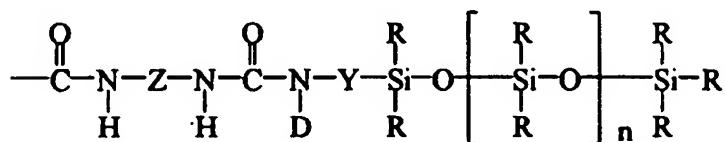


5

In the case of the diblock, X is hydrogen or has the structure:



10 In the case of the triblock, X has the structure:



In all of the structures presented above, D, Y, R, n, m, Z, A' and B' are defined as follows:

15 each D is individually selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, and a phenyl radical;

each Y is individually selected from the group consisting of an alkylene radical having from 1 to 10 carbon atoms, an aralkyl radical, and an aryl radical;

each R is individually selected from the group consisting of a monovalent alkyl radical having from 2 to 12 carbon atoms, a substituted alkyl radical having from 2 to 12 carbon atoms, a vinyl radical, a phenyl radical, and a substituted phenyl radical, with the proviso that at least 50% of the number of R radicals are methyl;

5 each n is an integer which is 5 or greater;

m is an integer which is 1 to about 25;

10 each Z is selected from the group consisting of aromatic, aliphatic, araliphatic and cycloaliphatic divalent radicals;

each A' is selected from the group consisting of -O-, -N- and -S- where G is

|
G

15 selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, a phenyl radical, and a radical which when combined with B' forms a heterocycle; and

each B' is selected from the group consisting of aromatic, aliphatic, araliphatic and cycloaliphatic radicals, polyethylene oxide, polypropylene oxide,

20 polytetramethylene oxide, polyethylene adipate, polycaprolactone, polybutadiene, polyamide, polysiloxane, mixtures thereof, and a radical completing a ring structure with A' to form a heterocycle.

It is noted that when D, Y, R, n, Z, A' and B' appear more than once in the diblock or triblock structure, they may be the same or different.

Preferably, each D is a hydrogen; each Y is selected from the group consisting of alkylene radicals having from 1 to 10 carbon atoms, more preferably having 1 to 3 carbon atoms, most preferably propylene; each R is methyl; each n is a number from 40 to 400; m is a number from 5 to 15; each Z 5 is individually selected from the group consisting of hexamethylene, methylene bis-(phenylene), tetramethyl xylylene, isophorone, tetramethylene, cyclohexylene, and methylenedicyclohexylene; and A' is selected from the group -N- and -O-.
10
11 |
 H

The present invention also provides release materials comprising these diblock and triblock copolymers and articles comprising said release materials. The article may comprise a backing having at least one layer of release material 15 applied thereto. The article may further comprise an adhesive layer coated onto the backing. The adhesive layer may be coated onto the side of the backing opposite the release material, or directly on the release material. The present invention also provides a laminate construction wherein a release liner is removably adhered to an adhesive article such as a tape. Preferably, the 20 adhesive is a rubber resin adhesive or other adhesive having a low acid content of less than about 2% by weight.

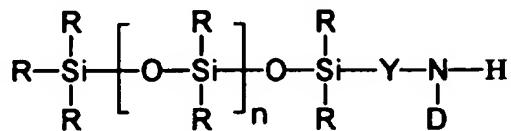
DETAILED DESCRIPTION OF THE INVENTION

The B-A diblock and B-A-B triblock copolymers of the present invention may be produced by mixing, under reactive conditions, a monoamine-functional 25 polydiorganosiloxane, a diamine and/or dihydroxy chain extender and a diisocyanate. The non-functional polydiorganosiloxane terminal segment is derived from the monoamine-functional polydiorganosiloxane, while the polyurea segment is derived from the diisocyanate and diamine and/or dihydroxy chain extender. The combined molar ratio of monoamine-functional 30 polydiorganosiloxane and diamine and/or dihydroxy chain extender to

diisocyanate in the reaction is that suitable for the formation of a block copolymer with desired properties. Preferably the ratio is maintained in the range of about 0.95:1.0 to 1.0:0.95, with 1.0:1.0 being most preferred.

Monoamine-functional Polydiorganosiloxane

5 The monoamine-functional polydiorganosiloxane has the following general structure:



wherein D, Y, R and n are defined above.

The monoamine-functional polydiorganosiloxane can be prepared by a variety of methods. A useful means of synthesizing such materials is via a platinum catalyzed hydrosilation reaction of a mono-SiH-terminated polydiorganosiloxane and an alpha-olefinic alkylamine compound. This method is described by Clouet et al. in Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 31, 3387-3396 (1993). Care should be exercised during the preparation of the monoamine-functional polydiorganosiloxane to avoid side reactions which could lead to undesired impurities in the material which will carry over into the final block copolymeric products. For example, -SiH groups may hydrolyze in the presence of water and the platinum catalyst to form silanol groups. These silanol functional polydiorganosiloxanes could be impurities which could adversely affect the elastomeric properties and release characteristics of the diblock and triblock copolymers formed. A discussion of the deleterious effects such silanol terminated species can have in elastomeric silicone-polyurea block copolymers can be found in U.S. Patent No. 5,290,615 (Tushaus et al.)

A preferred means of preparing the monoamine-functional polydiorganosiloxane can be found in U.S. Patent No. 5,091,483 (Mazurek et

al.). This method involves the use of an amine-substituted fluorosilane to terminate the anionic polymerization product of a cyclic siloxane monomer.

Diisocyanates

Any suitable organic diisocyanate, such as an aromatic, cycloaliphatic, 5 aliphatic, or araliphatic diisocyanate, may be used either alone or in mixtures of two or more. Suitable aromatic diisocyanates include 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, a dimer of toluene diisocyanate (available under the trademark Desmodur™ TT from Miles Coating Division), diphenylmethane 4,4'-diisocyanate (MDI), 1,5-diisocyanato-naphthalene, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, and mixtures thereof.

10 Examples of useful cycloaliphatic diisocyanates include dicyclohexylmethane diisocyanate (H₁₂MDI, commercially available as Desmodur™W from Miles Coating Division), isophorone diisocyanate (IPDI), 1,4-cyclohexane diisocyanate (CHDI), 1,4-cyclohexanebis(methylene isocyanate) 15 (BDI), 1,3-bis(isocyanatomethyl)cyclohexane (H₆XDI), and mixtures thereof.

16 Examples of useful aliphatic diisocyanates include hexamethylene 1,6-diisocyanate (HDI), 1,12 dodecane diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate (TMDI), 2,4,4-trimethyl-hexamethylene diisocyanate (TMDI), 2-methyl-1,5-pentamethylene diisocyanate, dimethyl diisocyanate, urea of 20 hexamethyl diisocyanate, and mixtures thereof.

21 Examples of useful araliphatic polyisocyanates include m-tetramethyl xylylene diisocyanate (m-TMXDI), p-tetramethyl xylylene diisocyanate (p-TMXDI), 1,4-xylylene diisocyanate (XDI), 1,3-xylylene diisocyanate, and mixtures thereof. Preferred diisocyanates, in general, include those selected 25 from the group consisting of isophorone diisocyanate, toluene diisocyanate, dicyclohexylmethane 4,4'-diisocyanate, 1,4-cyclohexane diisocyanate, m-tetramethyl xylylene diisocyanate, p-tetramethyl xylylene diisocyanate, derivatives of all the aforementioned, and mixtures thereof.

Chain Extenders

Suitable chain extenders include diamine and dihydroxy chain extenders. The chain extenders may be short chain diamines such as hexamethylene diamine, xylylene diamine, 1,3-di(4-piperidyl)propane (DIPIP), N-2-aminoethyl propylmethyldimethoxysilane (DAS), 1,3-diaminopentane (DAMP), 1,4-diaminopentane, piperazine, piperidyl propane and the like, with 1,3-di(4-piperidyl)propane and 1,3-diaminopentane being preferred. Examples of useful dihydroxy chain extenders include but are not limited to those selected from the group consisting of 1,4-butanediol, ethylene glycol, diethylene glycol, 10 dipropylene glycol, neopentyl glycol, 1,6-hexanediol, 1,4-cyclohexane dimethanol, and mixtures thereof.

Polymeric diamines as well as polymeric glycols may also be used. Useful polymeric diamines include those which have a functionality approaching 2.0 such as polyethylene oxide diamines; polypropylene oxide diamines; and 15 polytetramethylene oxide diamines having a molecular weight in the range of from 300 to 10,000, with a molecular weight in the range of 400 to 5,000 being most preferred. Such polytetramethylene oxide diamines and methods of making the same can be found in U.S. Patent No. 4,933,396 (Leir et al.). Other useful polymeric diamines are polyether diamines, sold under the tradename 20 JEFFAMINE, available from the Huntsman Chemical Co. Suitable polymeric diols include polytetramethylene oxide glycol, polyethylene oxide glycol, polyethylene adipate glycol, polypropylene oxide glycol, polybutadiene glycol, polycaprolactone glycol, and the like.

It is also possible to incorporate polysiloxane into the A segment of the 25 block copolymer by using a diamine or diol polysiloxane chain extender. These chain extenders typically have molecular weights of from about 500 to about 35,000, more preferably from about 1,000 to about 20,000. Examples of useful diol functional polysiloxane chain extenders include triblock copolymers comprising a polydimethylsiloxane midblock and a polyethylene oxide endblock

terminated with hydroxyl functionality. One such material is commercially available from Dow Corning Co. under the trade designation DC Q4-3667. Diamine functional polysiloxane chain extenders can be prepared by a variety of methods known in the art, most preferably according to the methods described in 5 U.S. Patent No. 5,214,119 and WO 95/03354.

The physical properties of the resulting block copolymer (such as tensile strength, hardness, abrasion resistance, glass transition temperature, flexibility, etc.) are affected by the selection of chain extender. In general, low molecular weight chain extenders may be used to increase the tensile strength, hardness and 10 abrasion resistance of the block copolymer, while polymeric diamines and polymeric glycols may be used to provide soft, flexible and elastic block copolymers. For example, when a diisocyanate is combined with large quantities of relatively low molecular weight chain extenders (preferably having a molecular weight less than 300), the hard character of the block copolymer is 15 enhanced and a leathery product may be obtained. By way of another example, when the block copolymer comprises high levels of polydiorganosiloxane and polymeric diamines or polymeric glycol chain extenders are used, soft or pliable materials are formed which may be used as sealants or additives. By way of yet another example, when diamine or diol polysiloxane chain extenders are used, 20 polysiloxane is incorporated in both the endblock and midblock segments of the resulting block copolymer. This allows for increased flexibility in tailoring release materials to provide a desired level of release. A discussion of the effects of various types of chain extenders on the mechanical properties of block copolymers may be found at page 172 in Abouzahr, S. and Wilkes, G.L. 25 "Segmented Copolymers with Emphasis on Segmented Polyurethanes" in Processing, Structure and Properties of Block Copolymers, Folkes, M.F., Elsevier, New York.

Preferably, the segments resulting from the chain extender comprise less than about 50% by weight of the copolymer formulation, depending on the properties of the resultant copolymer desired.

Preparation of Diblock and Triblock Polydiorganosiloxane-Polyurea Copolymers

5 The diblock and triblock copolymers of the present invention are prepared from the reaction of mixtures of monoamine-functional polydiorganosiloxane and chain extender, with approximately stoichiometric amounts of diisocyanate. The reactions are conducted in a dry solvent, or mixtures of solvents, protected from atmospheric moisture. The solvents are preferably unreactive with the
10 diisocyanates and chain extender. The starting materials and final products preferably remain completely miscible in the solvents during and after completion of the polymerization. Suitable solvents include polar liquids, such as alcohols, ethers, esters, and chlorinated hydrocarbons, with tetrahydrofuran and methylene chloride being especially useful. Preferred solvents are determined
15 by the nature of the reagents. For example, when all the reactants are amine functional and are reacted with aliphatic diisocyanates, secondary alcohols, such as isopropanol or 2-butanol, are preferred, either alone, or in combination with non-polar solvents such as toluene or cyclohexane. For reactions involving aromatic diisocyanates [e.g., diphenylmethane 4,4'-diisocyanate (MDI)],
20 tetrahydrofuran containing 10 to 25% of a dipolar aprotic co-solvent such as dimethylformamide is preferred.

25 The reaction conditions and procedures for preparation of the block copolymers will also vary depending upon the nature of the reactants. For reactions involving only amine functional starting materials, it is preferred to run the polymerization in two stages in order to ensure complete incorporation of the monoamine-functional polydiorganosiloxane("polysiloxane") into the final product. In the first step, the polysiloxane is added, either neat or in solution, to a solution of at least a fourfold molar excess of diisocyanate to provide a solution of a mixture of a polydiorganosiloxane ureido monoisocyanate and diisocyanate.

In the second step, the remainder of the diisocyanate, if any, is added, followed by a solution of the other diamine reactants. The preferred molar ratio of total amines to diisocyanates is in the range of from 0.95:1.0 to 1.0 to 0.95, most preferably in a ratio 1.0:1.0 in order to provide for maximum molecular weight 5 of the final block copolymer product. These reactions can be conducted at temperatures from 0 to 150°C. The reaction is preferably carried out at ambient temperature to 50°C. The reaction of amines with diisocyanates is exothermic, and no catalyst is required.

For compositions which incorporate diols into the formulation, a two 10 stage procedure for the preparation is also preferred. Again, it is preferred to add the polysiloxane to a solution of excess diisocyanate in a non-hydroxylic solvent, most preferably tetrahydrofuran. To this mixture is added the diols and a small amount of a catalyst such as stannous octoate or dibutyltin dilaurate, and heated at reflux for 1 to 2 hours, or until the reaction is complete. The preferred 15 molar ratio of amine plus diols to diisocyanates is 0.95:1.0 to 1.0:0.95. It is also possible to run the reaction initially at lower molar ratios of 0.70-0.90:1.0 to provide mixtures of isocyanate-terminated urethane oligomers. Polymerization is then completed by the addition of sufficient diamine chain extender to the reaction to bring the final amine/alcohol to diisocyanate molar ratio to 0.95-1.0: 20 1.0, most preferably 1.0 to 1.0.

The diblock and triblock copolymers of this invention can be prepared to have a wide range of useful properties by varying the weight ratio of segment B to segment A, the nature of the chain extenders and other polymers employed, and the molecular weight of the polysiloxane endblocks. The block copolymers 25 of this invention, for most applications, do not require curing to achieve their desirable properties, but yield tough solvent-cast films upon drying. When additional stability, solvent resistance or strength is desired, the silicone block copolymers can be crosslinked after casting or coating by any of the conventional methods known in the art, such as electron beam radiation, or use of peroxides.

The diblock and triblock copolymers of the present invention are suitable for use as release coatings for a variety of pressure-sensitive adhesives. They have good stability in solution, are film-forming, and have unusually high strength plus desirable mechanical and elastomeric properties. In addition, they 5 do not require high temperature curing or long processing times, a decided advantage in pressure-sensitive tape manufacturing.

The block copolymers of this invention may be prepared to give varying amounts of release through variations in the ratio of silicone segments to non-silicone segments (i.e. the ratio of B to A), the amount and nature of the chain 10 extenders employed, and the molecular weight of the polydiorganosiloxane block. In general, the amount of release can vary from 1.0 N/dm or less to about 35 N/dm. Certain copolymers are especially useful as low-adhesion backsizes (LABs) for pressure-sensitive adhesives tapes such as masking tapes. LABs for tapes in roll form typically exhibit release values in the range of from about 6 to 15 about 35 N/dm.

The preferred polydiorganosiloxane segment content for copolymers of the present invention used as release coatings for pressure-sensitive adhesives is from about 1 to about 50 percent by weight, the preferred ranges being dependent on the specific adhesive and its ultimate use. In general, thin film 20 coatings of copolymers comprising 1 to about 50 weight percent polydiorganosiloxane exhibit the necessary combination of adequate unwind on fresh tape with only a moderate increase in unwind force after adverse aging conditions of heat and humidity. For premium release coatings (i.e., release coatings having release values of less than about 2 N/dm), a higher content of 25 polydiorganosiloxane is required in the formulation, preferably from about 25 to 50 percent by weight polydiorganosiloxane. In applications where moderate release values are acceptable, the polysiloxane content may be reduced to lower levels, for example, 15% by weight and lower.

Typical number average molecular weights for the endblock of block copolymers intended for use in release materials are in the range of from 5,000 to about 30,000. The number average molecular weight of the midblock may vary over a wide range depending on the chain extender used to make this block.

5 The polysiloxane-polyurea diblock and triblock compositions of this invention, depending upon their viscosity, can be coated via any of a variety of conventional coating methods, such as roll, knife, or curtain coating, or extrusion coating. These compositions can be applied to at least a portion of at least one major surface of a suitable flexible or inflexible backing material and
10 dried to produce release-coated sheet materials. Useful flexible backing materials include paper, plastic films such as poly(propylene), poly(ethylene), poly(vinyl chloride), poly(tetrafluoroethylene), polyester [e.g., poly(ethylene terephthalate)], polyimide film such as DuPont's Kapton™, cellulose acetate, and ethyl cellulose. Backings can also be of woven fabric formed of threads of
15 synthetic or natural materials such as cotton, nylon, rayon, glass, or ceramic material, or they can be of nonwoven fabric such as air-laid webs of natural or synthetic fibers or blends of these. In addition, suitable backings can be formed of metal, metallized polymeric film, or ceramic sheet material. The coated sheet materials can take the form of any article conventionally known to be utilized
20 with PSA compositions, such as labels, tapes, transfer tapes (comprising a film of the PSA borne on at least one release liner), signs, covers, marking indices, and the like. Primers can be utilized, but they are not always necessary.
25

 This invention is further illustrated by the following examples which are not intended to be limiting in scope. Unless indicated otherwise, the molecular weights refer to number average molecular weights. All parts, percentages and ratios are by weight unless otherwise specified.

EXAMPLES

TEST METHODS

Aged Release Value

This test measures the effectiveness of the silicone release composition
5 after a period of heat aging. The aged release value is a quantitative measure of
the force required to remove a flexible adhesive tape from a substrate coated with
the test composition.

Aged release testing was conducted using a tape sample commercially
available from 3M Co. as general purpose masking tape no. 232. This tape
10 comprises a tackified natural rubber pressure-sensitive adhesive coated on a 1.27
cm wide resin impregnated crepe paper backing. The tape was rolled down with
5 passes from a 2 kg rubber roller onto a 2.54 cm by 25 cm strip of release
coated substrate prepared according to the following examples and allowed to
dwell in intimate contact for three days at 65°C. These laminates were then aged
15 for at least 6 hours at 22.2°C and 50% relative humidity and then adhered tape
side up to the stage of an Instrumentors, Inc. slip/peel tester (Model 3M90) with
double coated tape. The force required to remove the 232 masking tape at an
angle of 180° and a speed of 228.6 cm/min was measured.

Aged Readhesion

20 Aged readhesions were measured by adhering the freshly peeled tape
from the above test to a clean glass plate and measuring the peel adhesion using
the same Instrumentors slip/peel tester indicated above, again peeling at 228.6
cm/min and at a 180° peel angle, after allowing the test tape to dwell on the
glass plate for 30 seconds. These measurements were taken to determine
25 whether a drop in the adhesion value occurred due to undesirable contamination
of the adhesive surface by transfer of unincorporated silicone in the release
coating. Readhesions are reported as a percentage of the force required to
remove the aged sample from a clean glass plate versus the force required to
remove a control tape sample from a clean glass plate which has not been

adhered to the release coating. Preferably the readhesion values are 100% indicating no transfer of the silicone in the release coating to the tape. Readhesion values of about 80-90%, however, are acceptable.

Abbreviations

5	5K	Monoaminoalkyl-terminated polydimethylsiloxane having a theoretical molecular weight of 5,000
10	10K	Monoaminoalkyl-terminated polydimethylsiloxane having a theoretical molecular weight of 10,000
15	20K	Monoaminoalkyl-terminated polydimethylsiloxane having a theoretical molecular weight of 20,000
20	D400	Jeffamine TM D400, an α,ω -diaminopropyl poly(propyleneoxide) chain extender having an approximate number average molecular weight of 400, commercially available from Huntsman Chemical Co.
25	D4000	Jeffamine TM D4000, an α,ω -diaminopropyl poly(propyleneoxide) chain extender having an approximate number average molecular weight of 4000, commercially available from Huntsman Chemical Co.
30	DAMP	1,3-diaminopentane
35	DU700	Jeffamine TM DU700, an α,ω -diaminopropyl poly(propyleneoxide) chain extender containing internal urea groups having an approximate number average molecular weight of 900, commercially available from Huntsman Chemical Co.

	IPDI	isophorone diisocyanate
	M_n	number average molecular weight
5	5K DIAMINE	Diaminoalkyl-terminated polydimethylsiloxane having a theoretical molecular weight of 5,000

EXAMPLE 1**Preparation of Aminoalkyl Fluorosilane Terminating Agent**

10 A 500 ml, 3 neck round bottom flask was charged with 49.6 g 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 29.6 g ammonium fluoride, and 300 ml cyclohexane. While heating under reflux, water was removed by means of a Dean-Stark trap. After 18 hours, 4.4 ml of water had been collected, and the clear, colorless solution was transferred while warm to a 500 ml 1-neck round
15 bottom flask. The solvent was distilled on a rotary evaporator to provide 165 grams of white solid. This was dissolved in 200 ml of methylene chloride; 30 g of hexamethyldisilazane was added; and the mixture was stirred and heated under reflux for 5 hours. The flask was fitted for distillation and the solvent removed under aspirator vacuum. The product was distilled (boiling point of 70°C.) under
20 aspirator vacuum to provide 3-aminopropyldimethyl fluorosilane as a clear, colorless oil. The yield was 54 g (100%), which was determined to be pure by vapor phase chromatography. The structure was confirmed by NMR spectroscopy.

EXAMPLE 2**Preparation of Aminopropyl-Terminated Polydimethylsiloxane**

25 n -Butyl lithium (10 ml, 2.5 M) was added to 7.4 grams octamethylcyclotetrasiloxane under argon to form lithium silanolate initiator. After stirring for 30 minutes, a solution of 250 grams hexamethylcyclotrisiloxane in 250 grams dry tetrahydrofuran was added and the reaction stirred at room
30 temperature for 18 hours. To the resulting viscous syrup was added 3.4 grams 3-aminopropyldimethyl fluorosilane terminating agent described in Example 1.

The viscosity rapidly decreased. After stirring for 2 hours, the solvent was distilled off on a rotary evaporator. The product was filtered to remove lithium fluoride and provided 250 grams of silicone monoamine as a clear, colorless oil. Titration with 1.0 N HCl gave a number average molecular weight, M_n , of 9400 (theoretical $M_n = 10,000$). Using this procedure, but varying the reaction time and using a molar excess of terminating agent to cyclic siloxane, aminopropyl-terminated polydimethylsiloxanes of theoretical M_n of 5,000 (titrated number average molecular weight = 5,038) and 20,000 (titrated number average molecular weight = 19,274) were similarly prepared.

10 **EXAMPLE 3**

Preparation of Diblock and Triblock Polysiloxane-Polyurea

In an 100 ml round bottom flask, 0.10 gram of the aminopropyl-terminated polysiloxane macromonomer of Example 2 ($M_n = 9400$) and 2.9 grams JeffamineTM DU700 were combined. After heating this mixture to 100°C under 15 vacuum, 25 ml isopropyl alcohol were added to this mixture. In a second flask equipped with a mechanical stirrer, 5.02 grams of IPDI were mixed with 25 ml isopropyl alcohol. The contents of the first flask were then added to the contents of the second flask and the combined contents stirred for about 10 minutes. 1.98 grams of DAMP were then dissolved in 40 ml isopropyl alcohol 20 and added in one portion to the second flask. This mixture was stirred for several hours. Sufficient isopropyl alcohol was then added to result in a 5% solution of the block copolymeric product.

This 10% solids solution was then coated directly onto a 15.24 cm x 1 m strip of a 1.5 mil polyester film using a #6 Mayer rod and tested for release and 25 readhesion as described above. The results of these tests were recorded and can be found in Table I.

EXAMPLES 4-7

Block copolymers were prepared by the method of Example 3 by varying amounts of the aminopropyl-terminated polysiloxane, JeffamineTM DU700, IPDI

and DAMP in the polymerization mixture. The ratios of these starting materials are given in Table I. Release compositions were prepared and coated as in Example 3 except using a 5% solids solution. Release and readhesion test results are given in Table I.

5 EXAMPLES 8-9

To demonstrate the effect of molecular weight on the polydimethylsiloxane endblocks of the compositions of the present invention, two analogs of Example 5 were prepared using the lower molecular weight ($M_n = 5,038$) and higher molecular weight ($M_n = 19,274$) aminopropyl-terminated 10 polydimethylsiloxane starting materials of Example 2. The ratios of these starting materials are given in Table I. Release compositions were prepared and coated as in Example 3. Release and readhesion test results are given in Table I.

EXAMPLE 10

Example 10 illustrates the use of a higher molecular weight polymeric 15 chain extender, D4000. A mixture comprising 25 percent by dry weight of an aminoalkyl-terminated polydimethylsiloxane ($M_n = 9,257$), 50 percent by weight IPDI /DAMP, and 25 percent by weight D4000 was prepared, coated and tested according to the methods of Examples 8-9 except using a #3 Mayer rod. Release and readhesion test results are given in Table I.

COMPARATIVE EXAMPLE C-1

A segmented silicone-polyurea block copolymer was prepared using the method of U.S. Patent No. 5,214,119 (Leir et al.). The block copolymer comprised 20 percent by weight of a silicone diamine ($M_n = 10,000$) prepared according to the two-step method of U.S. Patent No. 5,214,119 using a tetramethylammonium silanolate catalyst, 60 percent by weight IPDI/DAMP and 20 percent by weight DU700. A release composition was prepared and coated as in Example 3. Release and readhesion tests were run and the results are in Table I.

10

Table I

Ex.	Poly-siloxane (wt %)	Jeffamine (wt %)	IPDI (wt %)	DAMP (wt %)	Aged Release Value (N/dm)	Aged Readhesion (%)
3	1	29(DU700)	50.2	19.8	36.3	92.2
4	3	27(DU700)	50.0	20.0	17.3	82.5
5	5	25(DU700)	49.9	20.1	12.0	105.0
6	20	20(DU700)	42.8	17.2	5.9	99.6
7	35	10(DU700)	38.6	16.4	1.5	97.3
8	5 (5K)	25(DU700)	50.0	20	10.5	87.8
9	5 (20K)	25(DU700)	49.9	20.1	11.5	90.4
10	25 (10K)	25 (D4000)	34.7	15.3	0.8	83.9
C-1	20 ¹	20(DU700)	43.1	16.9	10.0	99.2

¹Diaminoalkyl-terminated polysiloxane used instead of aminoalkyl-terminated polysiloxane macromonomer.

Table I illustrates that a full range of release characteristics were obtained through varying the amounts and molecular weights of the various components used to make the block copolymer of the present invention. Surprisingly, useful release coating compositions in the moderate to tight release range (i.e., release values in the range of 10-40 N/dm) were prepared using as little as 1-5 wt% polysiloxane macromonomer. Premium release values (i.e., release values less than 2N/dm) were observed for compositions having only 35 wt% of the monofunctional polysiloxane component. Such low release values are typically only seen in 100% silicone compositions. Furthermore, Example 6 and

5 Comparative Example C-1 clearly demonstrate the effect of different polymer architectures (B-A and B-A-B copolymers of the present application vs. (A-B)_n, segmented block copolymers of C-1) on release performance of coatings comprising the same amount of polydiorganosiloxane. At the same polysiloxane, diisocyanate and chain extender content, the copolymers of the present invention

10 possess a significantly lower peel adhesion than their segmented counterparts.

15

EXAMPLES 12-14

To further demonstrate the release properties of the compositions of the present invention, the coatings of Examples 8-10 were measured for release and readhesion as described above using an alternative tape sample (tackified styrene-isoprene-styrene (SIS) block copolymer adhesive on a polypropylene backing, commercially available as high performance box sealing tape no. 375 from 3M Co.). The results of these tests are recorded below in Table II.

Table II

Ex.	Polysiloxane (wt %)	Jeffamine (wt %)	IPDI (wt %)	DAMP (wt %)	Aged Release Value (N/dm)	Aged Readhesion (%)
12	5 (5K)	25(DU700)	50.0	20.0	5.8	79.6
13	5 (20K)	25(DU700)	49.9	20.1	15.9	80.6
14	25 (10K)	25(D4000)	34.7	15.3	1.2	79.2

Again, these examples show that a range of levels of release can be obtained for adhesives comprising tackified SIS block copolymers.

5 EXAMPLE 15

Preparation of an Organopolysiloxane Diamine Chain Extender

A solution of 14.79 g of bis-(3-aminopropyl) tetramethyl disiloxane and 352.9 g octamethylcyclotetrasiloxane was purged with argon for 20 min. and then heated to 150°C; 0.06 g (100 ppm) of 50% aqueous cesium hydroxide was added and heating continued for 6 hours until the aminopropyl disiloxane had been consumed. The reaction was cooled to 70°C, neutralized with excess triethylamine and acetic acid, and heated under high vacuum to remove cyclic siloxanes over a period of at least 5 hours. After cooling to ambient temperature and filtering to remove cesium acetate, an isolated diaminopropyl-terminated polydimethylsiloxane product was obtained having a theoretical molecular weight of 5,000 (titrated number average molecular weight = 5,276).

EXAMPLE 16

Example 16 demonstrates the use of the combination of monoaminopropyl-terminated polydimethylsiloxane of Example 2 ($M_n = 5,038$) and the silicone diamine chain extender of Example 15 ($M_n = 5,276$). These mixed aminopropyl functional polysiloxanes, each used in the proportion of 10 percent by weight, were combined as in Example 3 with 25 weight percent

polymeric chain extender D400 and 55 percent by weight IPDI/DAMP. These compositions were then coated and tested as in Example 3. The results of these tests are given in Table III.

Table III

Ex.	Polysiloxane (wt %)	Jeffamine (wt %)	IPDI (wt %)	DAMP (wt %)	Aged Release Value (N/dm)	Aged Readhesion (%)
16	10(5K) + 10(5K DIAMINE)	25 (D400)	41.8	13.2	2.3	94.6

5

This Example illustrates that near premium release levels may be achieved at low polysiloxane content (20 weight percent) by incorporating both polysiloxane endblocks and midblocks in the block copolymer by using both monoaminoalkyl - and diaminoalkyl-terminated polysiloxane starting materials.

10 **EXAMPLES 17-18**

Example 17 was prepared by making a block copolymer solution using the same procedure of Example 3 except for the use of both monoaminoalkyl-terminated polysiloxane ($M_n = 5,038$) of Example 2 and diaminoalkyl-terminated polysiloxane ($M_n = 5,276$) of Example 15.

15 Example 18 was prepared by making a block copolymer solution using the same procedure of Example 3 except for the use of both monoaminoalkyl-terminated polysiloxane ($M_n = 10,489$) made using the same procedure of Example 2 and diaminoalkyl-terminated polysiloxane ($M_n = 5,276$) of Example 15.

20 The block copolymer solutions were coated according to the procedure given in Example 3 and tested for release and readhesion using the procedure of Examples 12-14. Results of these tests are recorded below in Table IV.

Table IV

Ex.	Polysiloxane (wt%)	Jeffamine (wt%)	IPDI (wt%)	DAMP (wt%)	Aged Release Value (N/dm)	Aged Readhesion (%)
17	10(5K)+ 10(5K DIAMINE)	25 (D400)	41.8	13.2	1.8	80.8
18	10(10K)+ 40(5K DIAMINE)	0	34.8	15.2	1.6	80.4

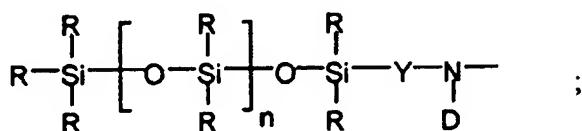
This Example illustrates that premium release levels may be achieved using polysiloxane contents of 20% and 50% when both the endblocks and 5 midblocks comprise polysiloxane.

WHAT IS CLAIMED IS:

1. A block copolymer having the structure B-A-X wherein B comprises a non-functional polydiorganosiloxane endblock, A comprises a polyurea block, and X is selected from the group consisting of hydrogen, a non-functional polydiorganosiloxane endblock, or an isocyanate radical.

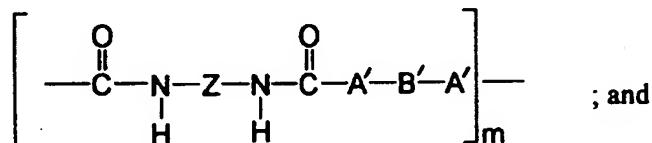
5 2. A block copolymer according to Claim 1, wherein:

B has the structure:



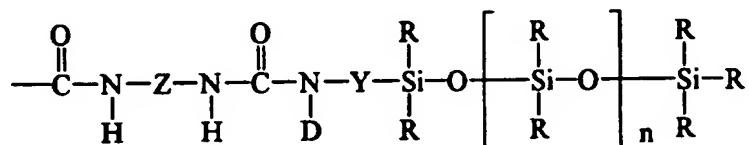
10

A has the structure:

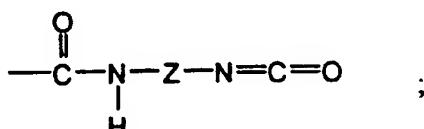


X is selected from the group consisting of hydrogen and the following structures:

15



and



20

wherein:

each D is individually selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, and a phenyl radical;

5 each Y is individually selected from the group consisting of an alkylene radical having from 1 to 10 carbon atoms, an aralkyl radical, and an aryl radical;

each R is individually selected from the group consisting of a monovalent alkyl radical having from 2 to 12 carbon atoms, a substituted alkyl radical having from 2 to 12 carbon atoms, a vinyl radical, a phenyl radical, and a substituted phenyl radical, with the proviso that at least 50% of the 10 number of R radicals are methyl;

each n is an integer which is 5 or greater;

m is an integer which is 1 to about 25;

each Z is individually selected from the group consisting of aromatic, aliphatic, 15 araliphatic and cycloaliphatic divalent radicals;

each A' is individually selected from the group consisting of -O-, -N- and -S-

|
G

where G is selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, a phenyl radical, and a radical which when combined with B' forms a heterocycle; and

20 each B' is individually selected from the group consisting of aromatic, aliphatic, araliphatic and cycloaliphatic radicals, polyethylene oxide, polypropylene oxide, polytetramethylene oxide, polyethylene adipate, polycaprolactone, polybutadiene, polyamide, polysiloxane, mixtures thereof, and a radical 25 completing a ring structure with A' to form a heterocycle.

3. A block copolymer according to Claim 2 wherein:

each D is hydrogen;

each Y is individually selected from the group consisting of alkylene radicals having from 1 to 10 carbon atoms;

30

each R is methyl;
each n is an integer from 40 to 400;
m is an integer from 5 to 15;
each Z is individually selected from the group consisting of hexamethylene, methylene bis-(phenylene), tetramethyl xylylene, isophorone, tetramethylene, cyclohexylene, and methylene dicyclohexylene; and
each A' is individually selected from the group consisting of -N- and -O-.

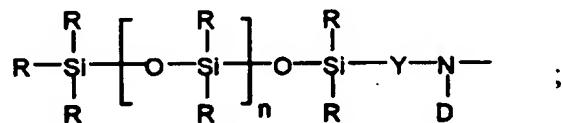
10 |
 H

4. A block copolymer according to Claim 3, wherein Y is propylene.
5. A block copolymer according to Claim 1, comprising from about
15 1 to about 50 percent by weight of said nonfunctional polydiorganosiloxane.
6. A block copolymer according to Claim 1, comprising from about
25 to about 50 percent by weight of said nonfunctional polydiorganosiloxane.
7. A block copolymer according to Claim 1, comprising less than 15
percent by weight of said nonfunctional polydiorganosiloxane.
20 8. A block copolymer according to Claim 1 prepared by reacting a
monoamine-functional polydiorganosiloxane, a chain extender and diisocyanate.
9. A block copolymer according to Claim 8, wherein said
diisocyanate is isophorone diisocyanate.
10. A block copolymer according to Claim 8, wherein said chain
25 extender is selected from the group consisting of diamine and diol chain
extenders and mixtures thereof.
11. A block copolymer according to Claim 8, wherein the combined
molar ratio of said monoamine-functional polydiorganosiloxane and said chain
extender to said diisocyanate is 0.95:1.0 to 1.0:0.95.

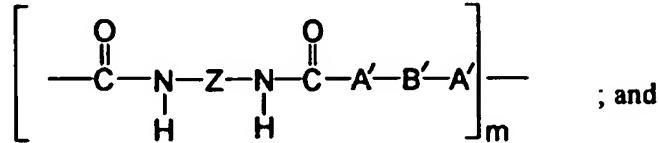
12. An article comprising a backing having at least one release material applied thereto, said release material comprising a block copolymer having the structure B-A-X wherein B comprises a non-functional polydiorganosiloxane endblock, A comprises a polyurea block, and X is selected from the group consisting of hydrogen, a non-functional polydiorganosiloxane endblock, or an isocyanate radical

5 13. An article according to Claim 12, wherein B has the structure:

10



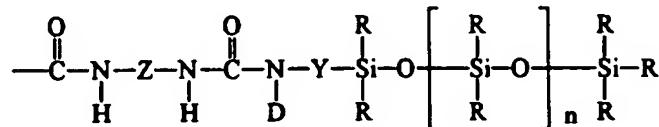
A has the structure:

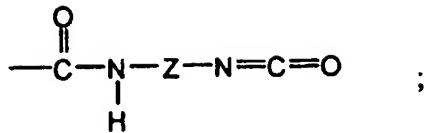


15 15 X is selected from the group consisting of hydrogen and the following structures:

20

and





wherein:

each D is individually selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, and a phenyl radical;

5 each Y is individually selected from the group consisting of an alkylene radical having from 1 to 10 carbon atoms, an aralkyl radical, and an aryl radical;

each R is individually selected from the group consisting of a monovalent alkyl radical having from 2 to 12 carbon atoms, a substituted alkyl radical having from 2 to 12 carbon atoms, a vinyl radical, a phenyl radical, and a substituted phenyl radical, with the proviso that at least 50% of the 10 number of R radicals are methyl;

each n is an integer 5 or greater;

m is an integer from 1 to about 25;

each Z is individually selected from the group consisting of aromatic, aliphatic, 15 araliphatic and cycloaliphatic divalent radicals;

each A' is individually selected from the group consisting of -O-, -N- and -S-

$$\begin{array}{c} | \\ \text{G} \end{array}$$

where G is selected from the group consisting of hydrogen, an alkyl radical having from 1 to 10 carbon atoms, a phenyl radical, and a radical which when combined with B' forms a heterocycle; and

20 each B' is selected from the group consisting of aromatic, aliphatic, araliphatic and cycloaliphatic radicals, polyethylene oxide, polypropylene oxide, polytetramethylene oxide, polyethylene adipate, polycaprolactone, polybutadiene, polyamide, polysiloxane, mixtures thereof, and a radical 25 completing a ring structure with A' to form a heterocycle.

14. An article according to Claim 12, wherein said backing comprises a material selected from the group consisting of paper, poly(propylene), poly(ethylene), poly(vinyl chloride), poly(tetrafluoroethylene), polyester, polyimide, cellulose acetate, ethyl cellulose, woven fabric and nonwoven fabric.

5 15. An article according to Claim 12, wherein said backing further comprises at least one layer of adhesive applied thereto.

16. An article according to Claim 15, wherein said adhesive is applied to said backing on a surface opposite to that of said release material.

10 17. An article according to Claim 15, wherein said adhesive is applied onto said release material.

18. An article according to Claim 12, removably adhered to an adhesive tape as a release liner.

15 19. An article according to Claim 12, wherein said block copolymer is prepared by reacting a monoamine-functional polydiorganosiloxane, a chain extender and diisocyanate.

20. An article according to Claim 19, wherein said diisocyanate is isophorone diisocyanate.

21. An article according to Claim 19, wherein said chain extender is selected from the group consisting of diamine and diol chain extenders and mixtures thereof.

22. A block copolymer according to Claim 8 wherein said chain extender is selected from the group consisting of diamine polysiloxane and diol polysiloxane chain extenders.

25 23. An article according to Claim 19 wherein said chain extender is selected from the group consisting of diamine polysiloxane and diol polysiloxane chain extenders.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/02083

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/80 C08G18/28 C08G77/458 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 274 103 (CHISSO CORP) 13 July 1988 see claims 1,9 see page 5, line 26 - line 48 see page 6, line 3 - line 10 ---	1
A	DE,A,39 38 963 (KANSAI PAINT CO LTD) 31 May 1990 see claims 1,3 see page 3, line 45 - line 64 ---	1
A	EP,A,0 250 248 (MINNESOTA MINING & MFG) 23 December 1987 see claims 1,4 & US,A,5 214 119 cited in the application & US,A,5 290 615 cited in the application -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 June 1996	02.07.1996
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Van Puymbroeck, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte: International Application No

PCT/US 96/02083

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0274103	13-07-88	JP-B-	6074330	21-09-94
		JP-A-	63161013	04-07-88
		US-A-	4822850	18-04-89
DE-A-3938963	31-05-90	JP-A-	2145673	05-06-90
		US-A-	5035934	30-07-91
EP-A-0250248	23-12-87	AU-B-	591989	21-12-89
		AU-B-	7447487	24-12-87
		JP-A-	63003029	08-01-88
		US-A-	5512650	30-04-96
		US-A-	5461134	24-10-95
		US-A-	5214119	25-05-93
		US-A-	5290615	01-03-94